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Blends of caprolactam/caprolactone copolymers and chlorinated polymers

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The phase behaviour of blends of chlorinated polyethylene, polyvinyl chloride (PVC) and chlorinated PVC with random copolymers of caprolactone and caprolactam has been investigated and the results correlated with a binary interaction model. The known miscibility of polycaprolactone in the chlorinated polymers is not compromised until a relatively high lactam content in the copolymer is attained. The incorporation of segmental interaction parameters, derived from separate studies involving polyamides, polyesters and their copolymers, has provided an estimate of the unknown parameters. Using only six parameters to account for experimental data has provided moderate success; however, it is clear that the representation of the chlorinated polymers, as pure copolymers of methylene ($-CH_2-$) and chlorine containing ($-CHCl-$) segments, is not sufficient to describe those blends. The reasons for this have been discussed in terms of the influence of configuration of species upon segmental interactions. Exploratory calculations are also presented depicting highly unfavourable interactions between aliphatic polyamides and chlorinated polymers and to describe how the window of miscibility in blends of the latter with semi-aromatic polyesters is affected by the methylene content of the polyester. © 1997 Elsevier Science Ltd.

(Keywords: chlorinated polymers; polyester; polyamides)

INTRODUCTION

The successful design of a polymer blend or multi-component system can now be placed on a more scientific basis than ever before. Simple binary systems form the primary objective of most blending operations; however, the underlying thermodynamic concepts and principles involved apply equally to polymers acting as surfactants at interfaces[1,2] and the manipulation of components in a blend to maximize rubber toughening technologies[3,4].

A major requirement to perform these tasks effectively is a measure of the interaction between different polymer backbones. Obtaining this information is not a simple procedure and although solubility parameter theories can be applied as a first approximation a more discriminating tool is required. There are methods available that estimate the favourable interaction between miscible components[5]. Unfortunately, there is great difficulty in trying to quantify the magnitude of an unfavourable interaction between different polymers. One solution to this problem, an example of which we will describe here, is by the use of copolymers and the application of a binary interaction model (BIM).

The use of BIMs[6–8] to describe the phase behaviour of a wide variety of polymer blends is now well established. The picture obtained is generally broad in nature and the model ignores some of the other features which contribute to the overall determination of mixing behaviour of polymers. Nevertheless, there is a strong predictive potential from the segmental interaction parameters which are derived from the semi-empirical application of the model to experimental systems. Accordingly, if a miscible polymer pair is chosen, where one of the components can be copolymerized, it is possible by the use of these random copolymers, and the determination of the interactional 'null' condition in blends with the second component, to quantify the unfavourable interaction between the latter and the polymer of the antagonistic comonomer. The particular example we will describe here involves blends of co-polyesteramides and chlorinated polyethylenes and PVC. Linear aliphatic polyester have demonstrated miscible behaviour with a wide variety of polymers[9–13]. Thus, by applying the known mixture relationships between polyamides, polyesters and their copolymers[14–16], it should be possible to define the unfavourable mixing relationships between polyamides and the chlorinated polymers by examining the phase behaviour of blends of the latter with co-polyesteramides. A complicating factor within this approach is that configuration of species and branching in the chlorinated polymers have been shown to influence phase behaviour involving blends of these materials[17–19]. We may

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Table 1 Composition and properties of chlorinated polymers

Polymer	Cl (wt%)	M_n ($\times 10^{-4}$)	M_w ($\times 10^{-4}$)	T_g, onset (°C)	T_g, midpoint (°C)	T_m (°C)	ψ_A[a]	ψ_H[a]
PE-C125	22.9	–	–	−27	−15	122	0.8156	0.1844
PE-C136	35.2	–	–	−22	−7	116	0.6849	0.3151
PE-C142	41.0	–	–	−22	1	n.o.	0.6126	0.3874
PE-C148	44.7	–	–	−16	6	n.o.	0.5621	0.4379
PVC	55.2	36	75	80	86	n.o.	0.3961	0.6039
CPVC67	66.4	43.5	85	112	124	n.o.	0.1704	0.8296

[a] Calculated from ref. 22 (see text)
n.o., not observed

Table 2 Composition and properies of caprolactam/caprolactone copolymers

Sample	Mol % LA	T_g, onset (°C)	T_g, midpoint (°C)	T_m,1 (°C)	T_m,2 (°C)	M_n ($\times 10^{-3}$)	M_w ($\times 10^{-3}$)	ψ_B[a]	ψ_D[a]
PCL	0	−70	−64	55	–	–	–	0	0.2302
6/4	3	−66	−60	57	–	4.8	29.9	0.0070	0.2233
8/1	9.3	−63	−58	55	211	13.3	44.0	0.0217	0.2088
6/5	11.8	−64	−60	57	–	1.4	23.6	0.0275	0.2030
3/6	12.8	−61	−55	55	–	29.0	78.0	0.0298	0.2007
6/2	17	−57	−46	55	–	3.0	22.4	0.0396	0.1910
3/1	19.4	−54	−40	57	–	n.a.	n.a.	0.0452	0.1855
8/7	23	−59	−54	53	211	19.8	54.8	0.0536	0.1772
8/5	34	−59	−55	41	210	17.2	75.8	0.0792	0.1518
6/8	35.6	−37	−30	66	–	1.5	21.8	0.0829	0.1481
6/7	40.3	−46	−40	51	–	1.5	21.4	0.0938	0.1373
8/4	42	−49	−43	44	212	18.1	69.3	0.0978	0.1334
8/2	44	−58	−55	47	212	15.8	81.5	0.1024	0.1288
4/4	44.1	−24	−15	81	–	28.0	82.0	0.1026	0.1285
3/8	51.1	−25	−18	52	210	33.0	94.0	0.1189	0.1124
4/3	68.1	2	10	–	137	28.0	92.0	0.1584	0.0733
5/3	86	13	23	–	193	31.0	101.0	0.1999	0.0322
PA-6	100	49	54	–	226	–	35.0	0.2324	0

[a] Calculated from ref. 22 (see text)
n.a., not available

therefore expect to encounter similar observations in the experiments described here.

EXPERIMENTAL

Materials

The preparation and characterization of the copolymers of caprolactam (LA) and caprolactone (LO) have been described in a previous communication[15]; however, a number of additional copolymers containing a higher proportion of LO were synthesized in order to provide a more comprehensive compositional range. Because of the difficulty in controlling reaction stoichiometry, and the formation of rather low molecular weight copolymers in high lactone copolymers, some polymerizations were performed using a small quantity (approximately 0.25 mol%) of activator (hexamethylene diisocyanate HMDI).

The poly(ϵ-caprolactone) (PCL), the four samples of chlorinated polyethylene, containing nominally 25, 36, 42 and 48 wt% chlorine, respectively, and the poly(ϵ-caprolactam), nylon 6, were obtained from Scientific Polymer Products. Characterization was performed on purified materials obtained as described below. PE-C125 and PE-C136, were purified by dissolving in *p*-xylene at 130°C, followed by centrifugation and precipitation in diethyl ether. PE-C142 and PE-C148 were treated similarly using THF/methanol and PVC and CPVC67 were subjected to a chloroform/*n*-hexane treatment. The PCL and copolymers (up to 20 mol% LA) were purified using chloroform or trifluoroethanol/chloroform, 1/1 v/v, as solvent (for copolymers with a LA content greater than 20 mol%) and precipitation in diethyl ether or *n*-hexane. Nylon 6 was subjected to a similar process with the TFE/chloroform (3/2 v/v) solvent mixture. All polymers were dried at 35°C under vacuum.

An independent determination of the chlorine content, performed by elemental analysis, indicated contents of 22.9, 35.2, 41.0 and 44.7 wt%, respectively, for the chlorinated polyethylenes. Poly(vinyl chloride) (PVC) was obtained from Pechiney et St Gobain (grade Lucovyl RB8010) and chlorinated PVC, CPVC67, was obtained

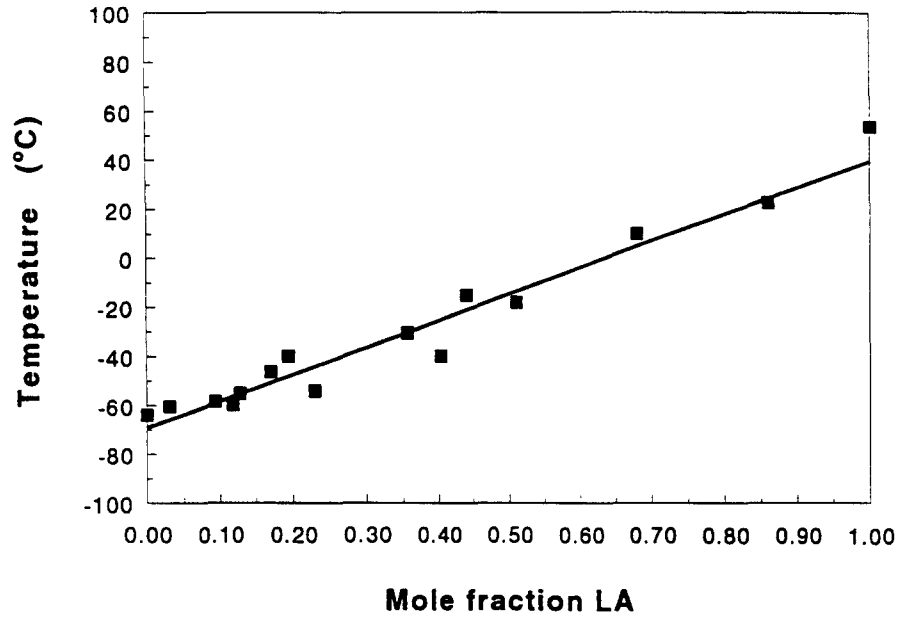

Figure 1 Measured and calculated (using the Fox equation) values of T_g (mid-point) as a function of composition of caprolactam/caprolactone copolymers

from Goodrich Temprite (grade Geon 674 × 571). Analyses of PVC and CPVC67 provided chlorine contents of 55.2 and 66.4 wt%, respectively. A summary of the compositional and thermal properties of the polymers referred to in this study is provided as *Tables 1* and *2*. All thermal properties reported were measured by conventional differential scanning calorimetry (d.s.c.) on quench cooled samples at 10°C min^{-1}. Compositional determination of the copolymers was performed by ^{1}H nuclear magnetic resonance (n.m.r.) using a mixture of $CDCl_3$ and hexafluoroacetone as solvent. Molecular weight determinations were performed by size exclusion chromatography (s.e.c.), using hexafluoroisopropanol as solvent, calibrated with poly(methyl methacrylate) standards.

Procedures

Blends were prepared by coprecipitation from a dilute solution (*ca* 2–3 wt%) of a common solvent, prepared by combining the two pure solutions, into an excess of the non-solvent diethyl ether. PE-C125 and PE-C136 were dissolved in *p*-xylene. PCL and copolymers containing less than 20 mol% LA were dissolved in tetrahydrofuran (THF). Those above 20 mol% LA were dissolved in warmed dimethyl sulfoxide (DMSO). Drying was effected at 35°C under vacuum.

Thermal characterization was performed using three techniques. The first of these consisted of a Perkin Elmer Series 7 (d.s.c.) equipped with a CCA7 controlled cooling accessory operating at a heating rate of 10°C min^{-1}. The glass transition temperature (T_g) was recorded both as the onset of the transition and the point of inflection of the heat capacity change at T_g. The melting point (T_m) was recorded as the maximum of the endotherm. A Rheometrics RSA II dynamic mechanical thermal analyser (d.m.t.a.), operating in the compression mode with a frequency of 1 Hz and a heating rate of 2°C min^{-1}, was applied to compression moulded samples (6 mm diameter; 1 mm thick).

We have also applied modulated d.s.c. to samples where overlapping exothermic (crystallization) and endothermic (T_g) processes have impeded the elucidation of phase behaviour. A TA instruments DSC2920 operating in the modulated temperature d.s.c. (m.t.d.s.c.) mode (average heating rate 2°C min^{-1}, period 60 s and amplitude 1°C) has been used to augment data from a Perkin Elmer DDSC operating under similar conditions. The underlying principles of this analytical procedure, and the data that can be obtained, are described in the literature[20,12].

Samples were equilibrated in the melt at 150 or 250°C and quenched in liquid nitrogen immediately prior to analysis. Analysis of vitrified blends is a very important precaution against some of the confusing consequences of crystallization. The criterion of a single T_g, intermediate between those of the two pure components, was used as the determinant of miscibility.

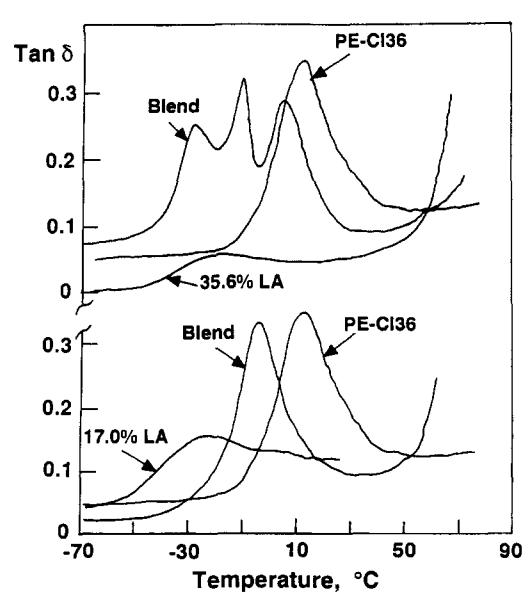

Figure 2 Representative dynamic mechanical spectra of blends (50/50) of PE-C136 with copolymers containing 35.6 (immiscible) and 17.0 (miscible) mol% LA, respectively, and the pure polymers

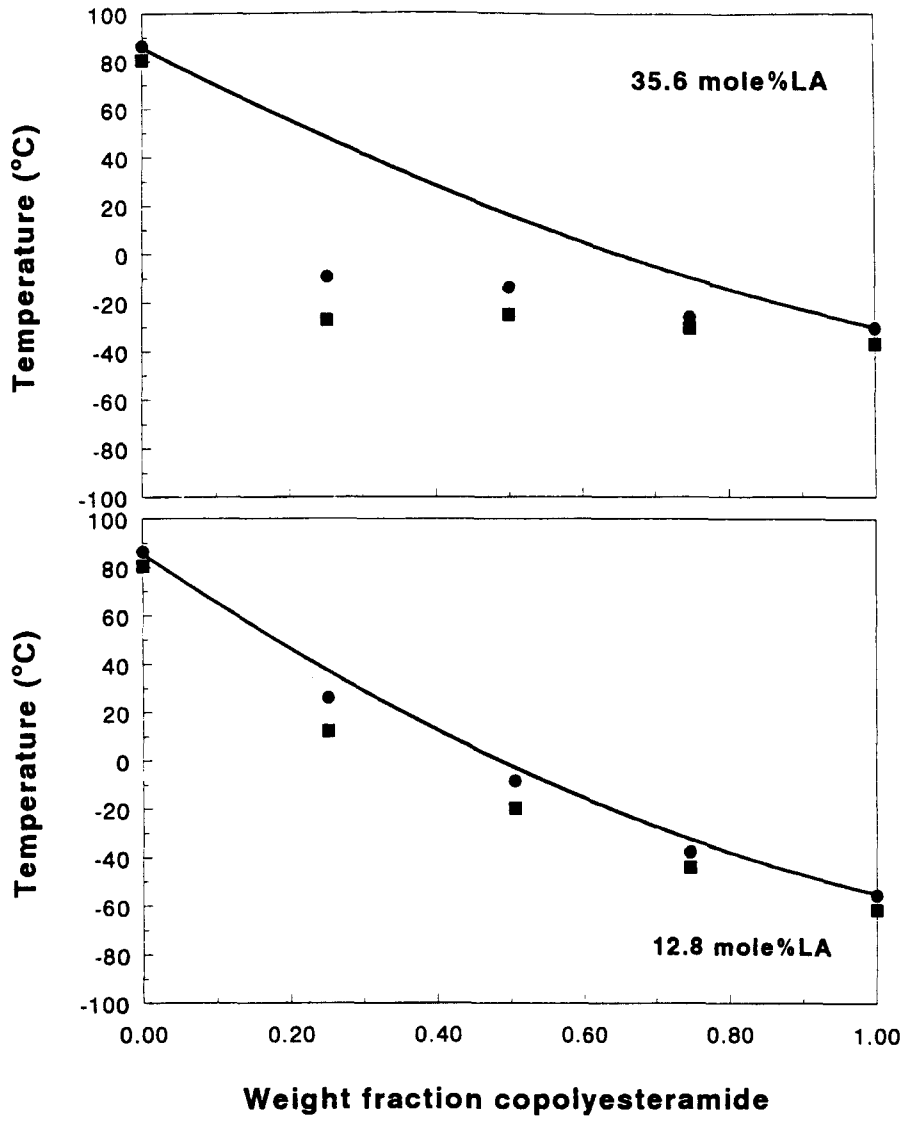

Figure 3 Summary of the measured T_g, as a function of blend composition, of blends of PVC with copolymers containing 35.6 (immiscible) and 12.8 (miscible) mol% LA, respectively; ●, onset; ■, mid-point. Drawn lines are calculated T_g (mid-point) from the Fox equation

RESULTS AND DISCUSSION

Blend studies

Several of the co-polyesteramides, notably those containing a high LA content synthesized using the HMDI activator, exhibited a small amount of 'blockiness', which was manifested by an additional small melting endotherm in a region (> 200°C) associated with that of nylon 6. Copolymers showing a strong secondary melting were rejected; however, in the remaining samples there appeared to be little influence either on copolymer homogeneity, as noted by the T_g, or on the phase behaviour of the blends that involved these copolymers. Although not all copolymers were utilized in blend studies, a summary of T_g, as a function of composition, is shown in *Figure 1*. The results support the formation of essentially random copolymers.

Phase behaviour of the blends has been determined by a combination of thermoanalytical techniques. Evidence in support of our conclusions concerning miscibility and immiscibility is presented in *Figures 2–5*, and a complete summary is presented in *Figure 6*. For example, *Figure 2* contrasts miscible and immiscible blends, demonstrated by d.m.t.a., formed by PE-C136 with the co-polyesteramides containing 17.0 and 35.6 mol% LA respectively. Samples formed for analysis by d.m.t.a. could not be quench cooled as efficiently as those prepared for d.s.c., and therefore contained some crystallinity. However, the additional peak observed in the d.m.t.a. trace for the blend containing 35.6 mol% LA is probably due to a small amount of additional crystallization rather than a relaxation from a third phase.

In some instances, studies have been extended across the range of composition. The information shown in *Figure 3* supports the inferred immiscibility of the blend of PVC with the copolymer containing 35.6 mol% LA. This figure also summarizes d.s.c. data for the miscible blend of PVC and the copolymer containing 12.8 mol% LA. The calculated T_g for the miscible blends is that described by the empirical Fox relationship. The thermograms on which these measurements are based are reproduced in *Figure 4*. The T_g of the miscible blend can be seen quite clearly to progress across the temperature scale as the blend composition changes. The immiscible blend demonstrates a small degree of cosolvency which we attribute to the presence of a distribution of species in the copolymer. Two widely

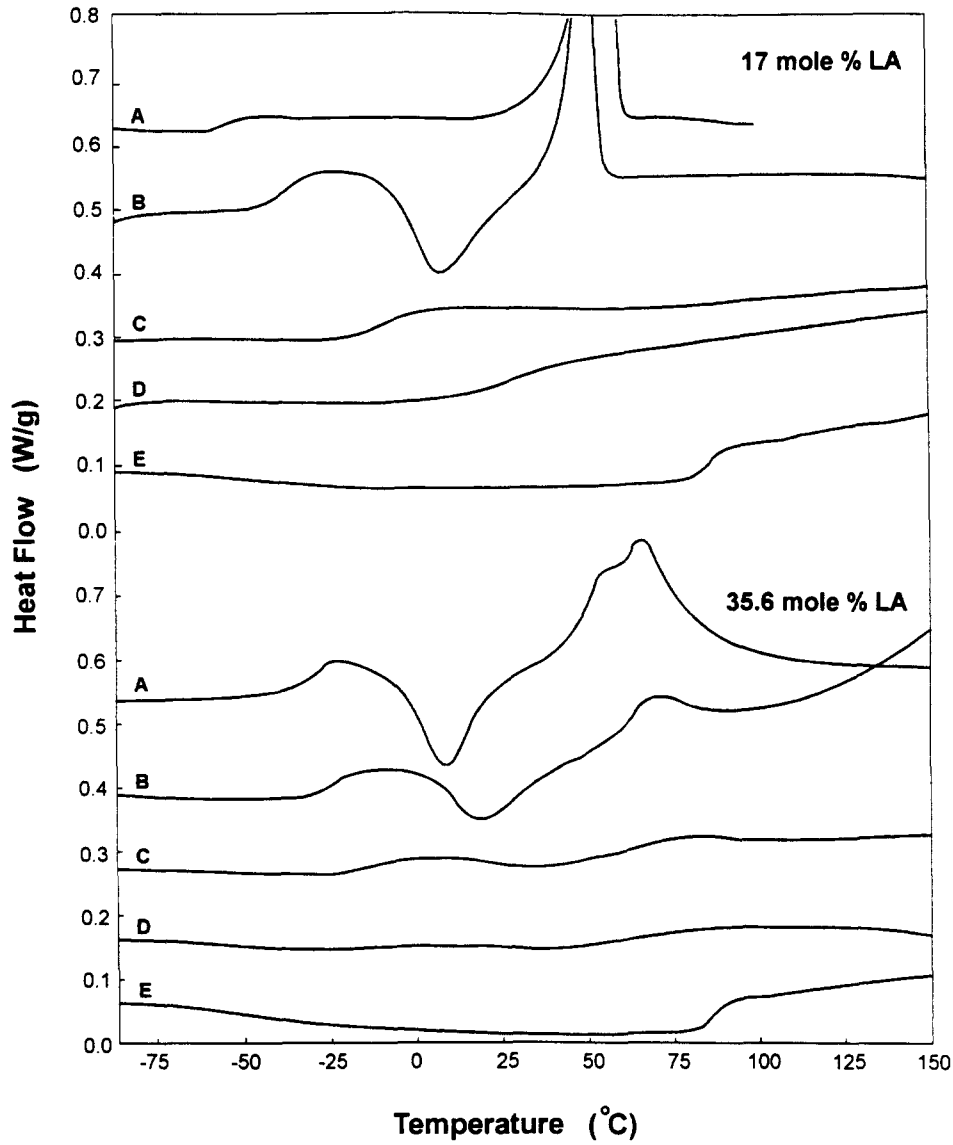

Figure 4 Representative thermograms of blends, of different composition, of PVC with co-polyesteramides containing 35.6 and 17.0 mol% LA, respectively. Blend composition LA/LO–PVC in wt% is: A, 100-0; B, 75-25; C, 50-50; D, 25-75; E, 0-100

separated T_gs are clearly visible, which do not support a conclusion of partial miscibility.

Figure 5 illustrates some of the advantages that dynamic d.s.c. offers when compared to the conventional mode of operation. The ability to separate reversible and non-reversible processes, in this case the cold crystallization of one of the blend components from an underlying glass transition, provides unique information on the apparent immiscibility of a blend of PE-C142 and a copolymer containing 34.0 mol% LA.

Theoretical section

A logical thermodynamic explanation of the observations noted above can be offered in terms of a binary interaction model. The premise upon which the model is founded is well documented; however, we will provide a brief summary as follows. Within a Flory–Huggins description of a binary polymer blend we define the free energy of mixing (ΔG) as:

$$\Delta G/RT = (\phi_1/N_1 \ln\phi_1 + \phi_2/N_2 \ln \phi_2) + \chi_{\text{Blend}}\phi_1\phi_2 \quad (1)$$

where N is the degree of polymerization and ϕ is the volume fraction of polymer in the blend. The interaction, χ_{Blend}, for a mixture of polymers 1 and 2 composed of different mers or segments, is an algebraic sum of the segmental exchange interactions, χ_{ij}. Represented in a simple form as equation (2), the segment volume fraction, ψ_i, is calculated from group contributions (ν_i) to the molar volume of polymers[22].

$$\chi_{\text{Blend}} = \sum \psi_i^1 \psi_j^2 \chi_{ij} - \left[\sum \psi_i^1 \psi_j^1 \chi_{ij} + \sum \psi_i^2 \psi_j^2 \chi_{ij}\right] \quad (2)$$

The first term represents unlike interactions between the two polymers, which are weighted according to the relative abundance of the various segments. The second term provides a summation of the repulsive interactions between unlike segments in the respective polymers. Interactions of like segments are give zero value.

As a first approximation, miscibility ensues when $\chi_{\text{Blend}} < 0$; however, for polymers of only moderate molecular weight, such as the copolymers described here, miscibility may still result for positive values of χ_{Blend}

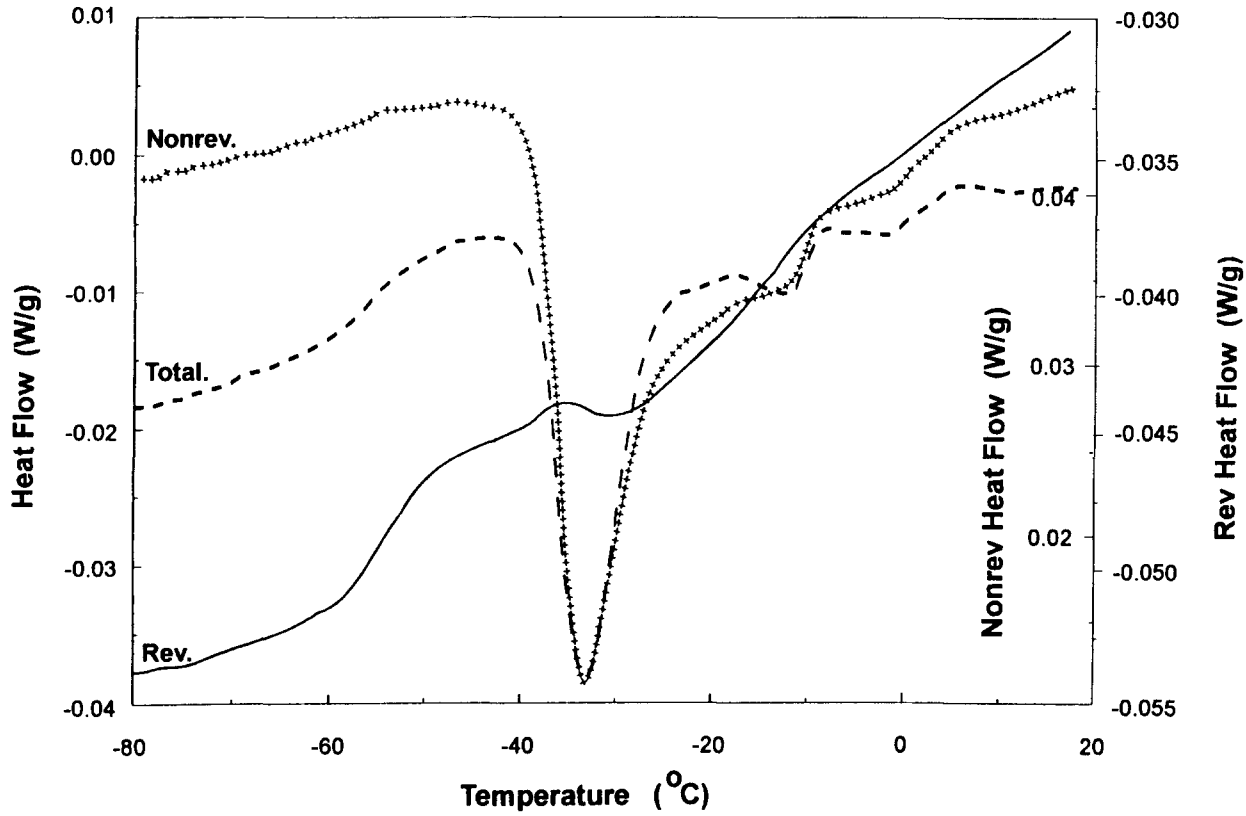

Figure 5 Representative thermograms, obtained by modulated d.s.c., of blends of PE-C142 and a co-polyesteramide containing 34.0 mol% LA

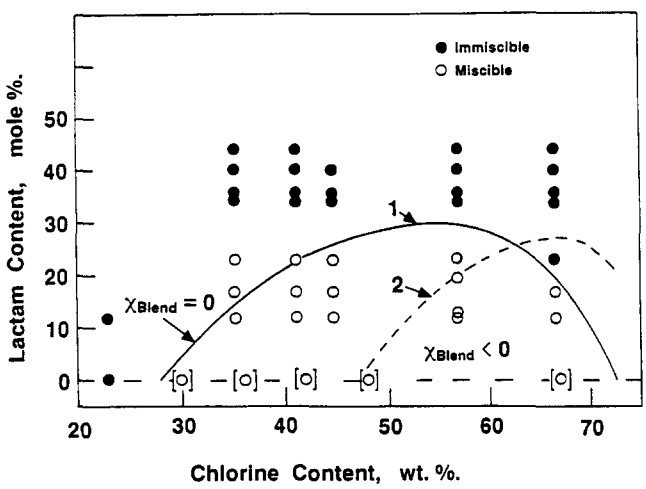

Figure 6 Comparison of experimentally observed phase behaviour and the application of the BIM model for blends of caprolactone/caprolactam copolymers and chlorinated polymers; [o] from refs 32, 33. 1: Locus of $\chi_{Blend} = 0$, obtained using $\chi_{AB} = 8.534$, $\chi_{AD} = 2.233$, $\chi_{BD} = 3.880$, $\chi_{AH} = 0.500$, $\chi_{DH} = 0.038$, $\chi_{BH} = 6.750$. 2: Locus of $\chi_{Blend} = 0$, obtained using $\chi_{AB} = 8.534$, $\chi_{AD} = 2.233$, $\chi_{BD} = 3.880$, $\chi_{AH} = 0.243$, $\chi_{DH} = 0.886$, $\chi_{BH} = 6.565$

that are less than a critical value, which depends on molecular mass in the usual way.

The simplicity of a BIM to qualify and quantify phase behaviour of polymer blends has encouraged its application to many different types of systems. The description obtained is invariably broad in scope and may begin to fail as the compositions of the polymers in question begins to depart strongly from those upon which the model parameters were originally founded. These deviations do not represent a fundamental inadequacy of the model, but rather a lack of suitable data available for inclusion in the calculations. The most notable refinement of the model since its introduction has been to try to accommodate the influence of configuration of segments. In this way, attention remains directed to a particular segment, but the adjoining segments allow differentiation of the interaction of a particular segment with other segments. Most treatments still assume that interactions between like segments have zero value, irrespective of their local environment.

Theoretical discussions[23–26] have been complemented by experimental investigations[17–19] with some degree of success. However it is difficult to separate the effects of local structure from other issues that have often been excluded to apply the analysis in the first place. Some studies[27–30] point to configuration of species as having a decisive effect on phase behaviour whereas others[16,31] have failed to detect any significant influence. The reasons for these differences probably reside with the chemical composition of the polymers in question and the proximity of the respective blends to an interactional 'null point'.

Application of the model

It is always desirable, whenever possible, to incorporate known behaviour and associated information in order to quantify structure/miscibility relationships between different polymer systems. Not only does this provide data that is obtained independently, but it also provides linkage with different studies and improves predictive capability. In view of previous publications, and the information they already provide, the most appropriate and consistent approach to adopt when attempting to fit the model to the systems at hand is to define segments in terms of the elementary species methylene (A), amide (B), ester (D), and

chloromethylene, CHCl, (H). The values of ψ_i have been calculated using[22] $\nu_A = 16.45\,cm^3\,mol^{-1}$, $\nu_B = 24.9\,cm^3\,mol^{-1}$, $\nu_D = 24.6\,cm^3\,mol^{-1}$, $\nu_{CHCl} = 28.25\,cm^3\,mol^{-1}$. Using this simple nomenclature six segmental interactions parameters are required to calculate χ_{Blend}. Four of these are available from previous work[15,17,18] ($\chi_{AB} = 8.534$, $\chi_{AD} = 2.233$, $\chi_{BD} = 3.880$, $\chi_{AH} = 0.092$). Therefore if two boundary conditions can be defined from the data shown in *Figure 6*, it is straightforward to derive the quantities χ_{BH} and χ_{DH}. Also included in *Figure 6* are data points from previous studies of PCL/chlorinated polymer blends[32,33].

In practice it has been found that by defining $\chi_{AH} = 0.092$, when used with the χ_{ij} noted above, fails to provide a tractable solution for all the data shown in *Figure 6*, regardless of the boundary conditions chosen. This does not mean that the latter quantity is in any way incorrect or erroneous. The discrepancy may be caused by a difference in the reference volume chosen by the two studies that were utilized to place the model on a lattice space basis rather than on a unit volume definition. Alternatively, it may also signify that our rationalization of these blends, as described above, is not sufficiently detailed enough.

We can expect that the interactions involving amide, ester and chloromethylene segments are relatively unaffected over most of the range of composition used here. These segments are always in the same local environment, that is, they are always centred in the same triads (ABA, ADA, AHA). However, this is not true for the interactions involving methylene segments. The situation is more complex when chlorinated PVC is included owing to the addition of AHH and HHH triads. Moreover, we have characterized the latter as a copolymer containing only A and H segments when in reality the polymer contains a small quantity of CCl_2 groups (approximately 6 mol%[33,34]).

There are several different approaches to try to overcome the problems noted above, each of which has its own associated approximations and drawbacks. Firstly, two critical miscibility limits can be estimated using the documented phase behaviour of PVC in aliphatic polyesters[35], and a third condition provided by establishing $\chi_{Blend} = 0$ for a blend of PVC and the copolymer containing 20 mol% lactam. The latter is an approximation using the data shown in *Figure 6*. The former conditions provide for miscibility of PVC in aliphatic polyesters ($-(CH_2)_nCOO-$) by defining $\chi_{Blend} = 0$ for $10 > n > 3$ ($\psi_A = 0.69$ and 0.86, respectively).

The solution derived from these calculations provides independent values for the critical limits for miscibility of PCL in chlorinated polymers and the miscible region as a function of lactam content. In the present scheme, a chlorine content of approximately 73.2 wt% represents the homopolymer –CHCl–. Although there is some uncertainty in establishing $\chi_{Blend} = 0$ for PVC in aliphatic polyesters, the solution obtained provides a poor description of the region of miscibility when compared to the data as shown in *Figure 6* (curve 2); however, the parameters derived obviously provide a good description of PVC in aliphatic polyesters as shown in *Figure 7*. The values of χ_{Blend} in the miscible region are appreciably negative, even though all segmental interactions are positive (endothermic). Miscibility is undoubtedly driven by an exothermic heat of mixing, consistent with previous studies involving calorimetry of

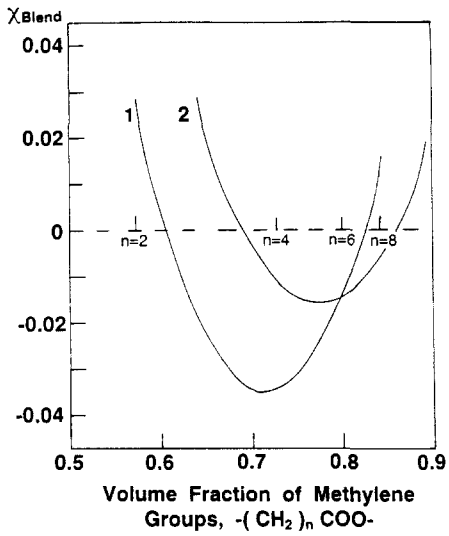

Figure 7 Values of χ_{Blend} for PVC in aliphatic polyesters. 1: Obtained using $\chi_{AD} = 2.233$, $\chi_{AH} = 0.500$, $\chi_{DH} = 0.038$. 2: Obtained using $\chi_{AD} = 2.233$, $\chi_{AH} = 0.243$, $\chi_{DH} = 0.886$

mixing model compounds[36], rather than entropically driven miscibility. An additional consequence of these calculations, although not shown here, indicates that the window of miscibility shifts to lower values of ψ_A as the degree of chlorination increases.

We propose that the deviations from calculated behaviour, for blends containing low levels of chlorination, can be attributed, in the main, to the dilution of HAH triads with AAA and AAH triads and the concomitant change in the magnitude of the interaction that occurs between these and other segments.

To account for the introduction of this level of complexity quantitatively requires more parameters in the calculation. For example, if it is argued that the environment of A in the chlorinated polymers has a relatively large effect on its interaction with other segments, then a minimum of three additional parameters are required. It is difficult to deconvolute which parameters are affected the most; however, if it is assumed that only χ_{AH} is influenced by composition, calculations indicate that a value close to that noted above ($\chi_{AH} = 0.092$) provides better agreement at low levels of chlorination. Recognizing that the value of χ_{AH} is influenced by the chlorine content of the chlorinated polymer in the blend, has been noted on a previous occasion[24].

An alternative to the computation outlined above requires defining critical values for miscibility of PCL in the chlorinated polyethylenes ($\chi_{Blend} = 0$ for blends of PCL in copolymers containing 28.0 and approximately 73 wt%, respectively, of chlorine) and a modification of the critical composition for the PVC/co-polyesteramide blend noted above, from 20 mol% LA to approximately 30 mol%. This fit of the data to the model (curve 1), as shown in *Figure 6*, provides the best solution when only six parameters are defined. If the entropic contribution to mixing is also taken into consideration, then the region of miscibility is slightly greater than that delineated by $\chi_{Blend} = 0$ in this figure, and we fail to account for only one data point. A further consequence of the latter fit of the model is the inability to describe accurately, the miscibility window of PVC in aliphatic polyesters. This result is shown in *Figure 7*, which also

illustrates how the values of χ_{Blend} in the miscible region assume even greater negativity.

The principal difficulty in trying to quantity the picture at hand is that we are trying to rationalize several complex blend systems using only six parameters. For example the chlorinated polymers are not perfect CH_2/CHCl copolymers and both of the approaches described above exclude any influence that can be attributed to configuration of segments. This may be particularly influential in blends where the local environment of segments varies enormously. In PVC all A segments are in a HAH configuration, whereas in PE-C132 relatively few are. In all probability, the behaviour of PVC and a chlorinated PE of equivalent chlorine content, will behave in a significantly different manner.

Finally, we could also offer a different nomenclature by defining the chlorinated polymers in terms of A and H′ segments, where H′ represents a CH_2–CHCl segment; however, using this notation PVC represents the homopolymer that would exclude chlorinated PVC from consideration. An evaluation of the data using this scheme may be useful for investigating copolymers of PVC, such as vinyl acetate copolymers.

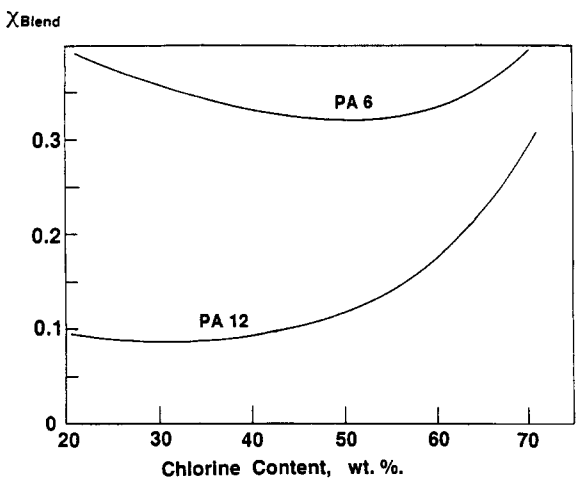

Figure 8 Calculated values of χ_{Blend} for blends of chlorinated polymers with nylon 6 and nylon 12, respectively. Obtained using $\chi_{AB} = 8.534$, $\chi_{AH} = 0.500$, $\chi_{BH} = 6.750$

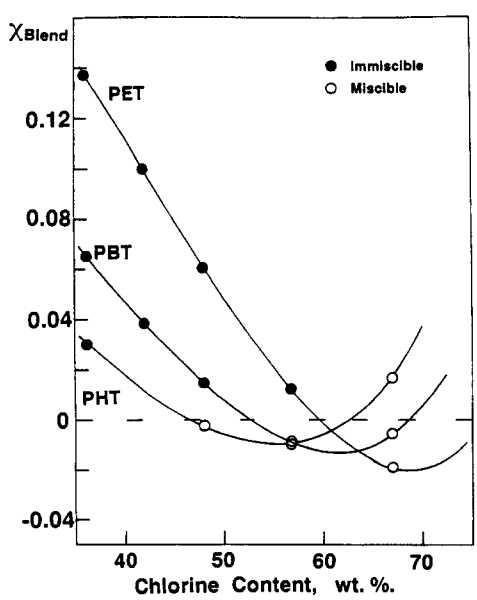

Figure 9 Comparisons of calculated values of χ_{Blend}, for blends of chlorinated polymers with semi-aromatic polyesters obtained using $\chi_{AD} = 2.233$, $\chi_{AH} = 0.500$, $\chi_{DH} = 0.038$, $\chi_{AC} = 0.1$, $\chi_{CD} = 1.692$, $\chi_{CH} = 0.68$, and experimental data obtained from refs 38–40

Application to blends of chlorinated polymers with aliphatic polyamides and semi-aromatic polyesters

As noted in our introductory remarks, an important outcome of undertaking these studies is to examine the predictive potential of the segmental interaction parameters deduced, and hence provide linkage to related polymer blends. The exercise should always be viewed as speculative; however, the information obtained invariably provides a sensible description of behaviour and stimulates additional areas of investigation.

The extraction of an estimate for the segmental interaction parameter χ_{BH} permits calculations of χ_{Blend} for blends of aliphatic polyamides in chlorinated polymers. Examples for nylon 6 and nylon 12, respectively, are shown in *Figure 8*. Not surprisingly the results indicate a highly unfavourable interaction, irrespective of chemical composition, which moderates slightly as the methylene content of the polyamide increases. The parameters used to calculate the data shown in *Figure 8* are the same as those which form the basis for deriving curve 1 in *Figure 6*, and therefore are probably more applicable to blends involving chlorinated PE. For blends based upon PVC, the parameters involved in deriving curve 2 in *Figure 6* are more appropriate. Although not shown, the general trends are unaffected and values of X_{Blend} of 0.233 and 0.053 are obtained for blends of PVC with nylon 6 and nylon 12, respectively (c.f. values of 0.325 and 0.150, respectively, from *Figure 8*).

Blends of chlorinated polymers with semi-aromatic polyesters (ACD polymers; C is a phenyl group), such as poly(butylene terephthalate) (PBT), have received much less attention than their aliphatic counterparts. Nevertheless, evidence suggests that blends of these materials are also capable of displaying a window of miscibility that depends upon the chlorine content. We are able to accommodate such behaviour in the same way as that described above provided that the appropriate segmental interaction parameters are available.

Separate studies[27,37] have indicated that $\chi_{AC} = 0.1$ and $\chi_{CD} = 1.692$ are suitable approximations for two of the three additional parameters required to calculate χ_{Blend}. The value of χ_{CH} is unknown; however, it is instructive to demonstrate a fit of the model based upon a sensible estimate of the latter ($\chi_{CH} = 0.68$). Only a small adjustment (± 0.04) of the latter parameter induces a poor correlation of data with the calculations. Shown in *Figure 9*, the estimated values of χ_{Blend} compare very favourably with information reported in the literature[38–40]. As the methylene content of the polyester increases, the model describes quite accurately a shift of the miscibility window to polymers with a lower chlorine content. It is also worth noting that the similarity of the magnitude of the parameters χ_{CH} and χ_{AH} is a trend consistent with previous observations involving the interaction of A and C segments with different species, e.g. amide and ester groups, respectively.

The parameter used to calculate the information in *Figure 9* included those formulated to give the best fit

for chlorinated polymers as described above. We need to emphasize that such calculations are based on a simple scheme and should be viewed only as tentative. For example, the parameters χ_{AC} and χ_{CD} are derived from studies involving segments in a very different chemical environment. Similarly, the computation does not take into account any change in the magnitude of the interaction of ester groups that may result from the change of configuration from an aliphatic to an aromatic environment. Nevertheless, we are able to capture the essential behaviour of these blends. Similar procedures are also capable of showing highly unfavourable interactions between chlorinated polymers and semi-aromatic polyamides of analogous chemical structure, e.g. poly(hexamethylene terephthalamide), Nylon 6T.

CONCLUSIONS

Miscible blends of chlorinated polyethylenes and PVC, respectively, with aliphatic co-polyesteramides can tolerate a relatively large proportion of lactam, in a copolymer of a lactone, without inducing phase separation. The application of a binary interaction model, in its most elementary form, has allowed for a description of the data in terms of segmental interaction parameters involving simple structural units, e.g. amide groups, methylene groups etc. There has been difficulty in obtaining exact agreement between experimental behaviour and predictions for all blend systems that can be defined in terms of the parameters obtained from this study. We have shown that these discrepancies, in common with other studies involving chlorinated polyethylenes, may be attributed to the effects of configuration of segments in these polymers and the fact that they are not perfect methylene/chloromethylene copolymers. Accordingly, with regard to our initial objective of being able to demonstrate the use of copolymers to estimate interactions in polymer blends, chlorinated polymers of the nature used here are perhaps not the most amenable to such treatment.

The three unknown parameters required to define the systems here, in common with the three already available from other studies, have all been found to be positive and unfavourable for homogeneous mixing. The interaction between amide and chloromethylene segments is highly unfavourable for homogeneous mixing. Additionally, the apparent slightly repulsive interactions between ester and chloromethylene segments contrasts with the unfavourable specific interaction, presumably negative and exothermic, which has often been proposed as the promoting influence for miscibility in PVC with aliphatic polyesters. However, care must be exercised when placing physical significance on the sign of a segmental interaction parameter, since they may easily be affected by reference quantities that are used to construct the model. Accordingly, the application of the current parameters to other systems should be approached with care. Nevertheless, we have used this information to extrapolate the behaviour of chlorinated polyethylenes, PVC and CPVC in polyamides. The expectation of grossly incompatible systems, denoted by large positive values of the interaction between these polymers, has been supported by independent calculations based upon the segmental interaction parameters obtained here.

We have also provided calculations illustrating how the same parameters, reported here and in the literature, are capable of predicting a miscibility window in blends of chlorinated polymers with semi-aromatic polyamides, such as poly(butylene terephthalate). The principal reason for the apparent success of this simple model to describe the phase behaviour of these types of blends is related to the large contrast in chemical nature of the segments comprising the polymers involved and the fact that only minor changes in the relative proportions of these segments dominate the thermodynamics of mixing.

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